Journal of Optoelectronics and Advanced Materials, Vol. 3, No. 2, June 2001, p. 389 - 394

EFFECTIVE HOLOGRAPHIC RECORD ON THIN FILMS OF CHALCOGENIDE SEMICONDUCTORS

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In this work is presented the research on thin films of chalcogenide glassy semiconductors as the medium for relief holograms record. The optimization of photoresist has allowed for an an essential rise in sensitivity to light. $As_{50}Se_{50}$ photoresist composition on which above thousandfold chemical amplification of holographic record is achieved, was used. Diffraction gratings in range of spatial frequencies 600 - 2400 mm^{-1} are submitted. For natural light the magnitude of diffraction efficiency exceeds 70 - 80 % at measurements in autocollimator conditions. The probable cause of differences between continuous and pulse irradiation of thin films of chalcogenide vitreous semiconductors is discussed.

(Received June 6, 2001; accepted June 11, 2001)

Keywords: Photoresist, Reflective holographic diffraction grating, Thin film, Chalcogenide vitreous semiconductors

1. Introduction

The change of optical, physical and chemical properties of thin films of chalcogenide vitreous semiconductors (ChVS) under the influence of a band-gap irradiation is a subject of research during more than 30 years. One of the directions of such researches is the analysis of photoresistive properties [1-4]. The materials from this class was investigated also as electron-beam [5] X-ray [6] and ion-beam resists [7]. As a result of actinic irradiation and subsequent chemical treatment, were obtained structures for microlithography, for the production of holographic diffraction elements, kinoforms and optoelectronic elements [1-9].

The photoresistive properties of the whole class of ChVS thin films were studied. Chemical increase of phase component of an optical record resulted into reduction of exposure necessary for maximum diffraction efficiency. This is equivalent to the increase of material sensitivity. The task to work out photoresistive process was solved not for all investigated structures [10]. A broad spectrum of the characteristics of such inorganic photoresists was obtained [1-4, 8-11]. However it is impossible to consider that the optimization of the photoresists of this type is reached.

The selection of structures for research as photoresists is connected, first of all with the value of photoinduced changes in optical constants. Usually the exposure of ChVS thin films to optical irradiation from a continuous source is investigated. There are few works that report the results of a pulse illumination of such registering medium [12-14]. The parameters of photoresists on the basis of ChVS after the pulse action were not considered by other authors.

The purpose of the present work was the research photoresistive properties for several compositions of thin ChVS films. As a result of the preliminary analysis for optimization the binary structure As-Se is selected. Two regimes of exposure were investigated: continuous and pulse ones. For both cases the reflective holographic diffraction gratings are obtained. In this work their parameters are presented. On the basis of our views on optical record mechanism in the thin ChVS films and available experimental data, the observed difference in sensitivity for a continuous and pulse exposure is discussed.

2. Experimental

For experiments thin ChVS films of several compositions were selected. The initial bulk glasses were synthesized in the vacuum-evacuated quartz ampoules. The thin films were produced by a thermal deposition in vacuum 10^{-3} Pa onto oxide glass substrates. For the production of holographic diffraction gratings the specially produced glass plates with high surface quality were used. The thickness during deposition was controlled by an interference method on a wavelength outside of area of ChVS sensitivity (λ = 1.15 μm). The uniformity of thickness was reached due to the planetary rotation of samples during deposition. The evaporation was from tantalum effusion cells. The velocity of evaporation was 50-70 Å/s. The composition of initial ChVS and vapour-deposited film was controlled by electron microprobe X-ray spectral analyses. The deviation for As-Se films did not exceed 2 at. %. The holographic diffraction gratings were recorded according to the symmetrical scheme of a double-beam interferometer. The flatness of registration of an interference pattern was set normal to bisectrix of angle between the light beams. In the result the sinusoidal distribution of an interference pattern was converted into a surface relief with a symmetrical profile. The continuous record was carried out on the two wavelengths of the Argon-ion laser (0.48 and 0.51 μm). For a pulse record the phosphate neodymium glass laser irradiation was used. The exposure was made by single-pulses with duration 40 ns on the wavelength 0.53 μm. Besides, the processes of optical record were investigated on wavelengths of He-Ne laser (0.63 μm) and Cu laser (0.51 μm) with pulse repetition frequency 9 KHz. In some cases the dye laser was applied and the wavelength range 0.45 - 0.60 μm was investigated.

In the work we used successive and simultaneous effect of optical irradiation of two wavelengths on one and the same film area. Thus the radiation with the greater wavelength was entered into a film with the help of prism coupling element [15,16].

3. Results and discussion

The maximum ChVS thin films etching selectivity of a number of compositions are given in the Table 1. The selectivity was determined as a velocity ratio of etching of the exposed and not exposed film areas. The exposure was carried out until saturation. All the presented photoresists in the selected conditions of processing by organic alkalis (water and aqueous-alcoholic solutions of amines) were negative.

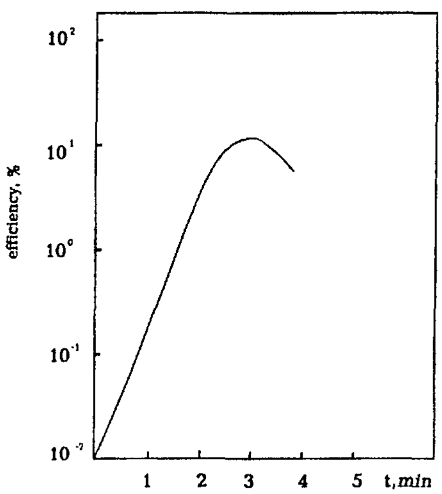

Fig. 1. Diffraction efficiency versus etching time in $As_{50}Se_{50}$ thin films. The best results were got on $As_{50}Se_{50}$ thin films.

Table 1. Experimental values of etching selectivity for some photoresistive ChVS Thin Films.

Composition	Selectivity
$Ge_{22}As_{20}Se_{58}$	5
$Ge_{25}As_{11}Se_{64}$	2
$As_{30}S_{70}$	25
$As_{40}S_{60}$	20
$As_{20}S_{80}$	4
$As_{30}Se_{70}$	5.3
$As_{50}Se_{50}$	60
$As_{40}Se_{60}$	9.3

The films of such composition under irradiation of He-Ne laser (0.63 μm) show considerable changes of optical constants [17]. The comparison of the results of the first record cycle and the subsequent ones demonstrates magnitude comparability of reversible and irreversible changes of optical constants [17]. At application of such ChVS film as a photoresist, the necessity for a preliminary annealing disappears, because both components give the contribution to resultant sensitivity. The selectivity of etching on the annealed film essentially decreases. On as-evaporated $As_{50}Se_{50}$ film the considerable strengthening of a diffraction grating recorded by irradiation of He-Ne laser is reached. In Fig. 1 is shown the dynamics of diffraction efficiency change during etching. The initial value of diffraction efficiency increased, and in a maximum it reached 18 %.

During recording under irradiation from shorter wavelength spectrum area, the sensitivity of the ChVS film increases, but the effective depth of light interaction with material, however, decreases. Therefore, characteristics of a usual amplitude-phase record at such transition is aggravated. At the use of photoresistive process the selectivity of etching of a surface amplitude-phase mask can compensate this drawback. Considerable increase of sensitivity of medium can be reached in this way. The reflective diffraction gratings were obtained in the field of spatial frequencies 600 - 2400 mm^{-1}. Samples by the sizes 200x200 mm are experimentally obtained. The energy density of an exposure was in the interval 0.01 - 0.03 J/cm^2. The smaller value corresponds to as-evaporated samples, for which the sensitivity drops as a result of relaxation processes [18].

In Fig. 2 and 3 is shown the spectral dependence of diffraction efficiency of reflective diffraction gratings obtained on $As_{50}Se_{50}$ thin films. The diffraction efficiency in the first diffraction order according to auto-collimation scheme [19] was measured. In Fig. 3 besides the results for natural light (curve 3), the values of diffraction efficiency for two polarizations of irradiation are shown: with an electric vector, directed normally (H–polarization, curve 1), and parallel (E–polarization, curve 2) to the grooves of a grating.

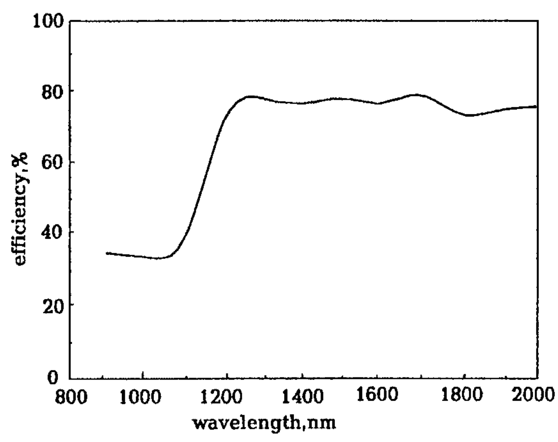

Fig. 2. First order diffraction efficiency of refractive holographic grating (spatial frequency 600 mm^{-1}) in As_{50} Se_{50} thin films versus wavelength.

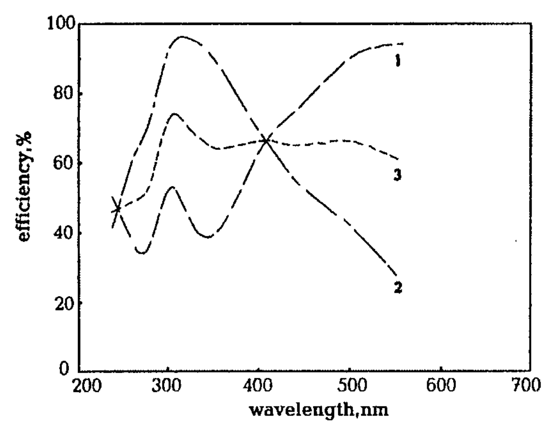

Fig. 3. First order diffraction efficiency of refractive holographic grating (spatial frequency 2400 mm^{-1}) in As_{50} Se_{50} thin films versus wavelength.

In the paper [19] it was shown, that the diffraction efficiency of a grating with a sinusoidal profile is maximum at the altitude of grooves equal 0.3 - 0.4 from the value of grating period.. Thus, if the depth of a relief makes 0.3 from the value of the period, the clearly seen maximum is watched in the field of low wavelengths. If the depth of relief makes 0.4 from the value of the period - broad plateau is seen [19]. All other analysed in the work [19] symmetrical profiles of grating grooves are characterized by sharper spectral maximums of diffraction efficiency. It is possible to conclude, that in all range of spatial frequencies the diffraction gratings with grooved profile, close to sinusoidal and optimum relief altitude, are obtained in $As_{50}Se_{50}$ thin films (see Fig. 2 and Fig. 3). The record of high frequency gratings (2400 mm^{-1}) was made on 0.48 μm wavelength, and the rest of gratings (600 and 1200 mm^{-1}) - on 0.51 μm wavelength of Argon-ion laser.

The maximum of diffraction efficiency of the obtained diffraction gratings in natural light reached 70 - 80 %. Chemical strengthening and transition to record in smaller wavelengths area allowed to increase essentially the medium sensitivity.

Earlier we conducted researches of temperature relations of photoinduced changes of optical constants and effect of thermo-optical erasure on ChVS thin films [17,18]. The conclusion was drawn, that under the influence of actinic light the definite state that corresponds to conditions of exposure and temperature is established each time in the material. The transition between any such states can be carried out by temperature variation of recording media. There can be any direction of transition: additional record, if the medium temperature decreased, or erasure by the same irradiation, if temperature of ChVS thin film increase. So, in such materials during exposure aiming for record the opposite process, erasure, takes place. The saturation of photoinduced changes occurs, when processes of a record and the erasures balance each another. The equilibrium can be shifted in any direction.

Later, in the work [12], the increase of sensitivity of ChVS thin films was revealed for a pulse exposure. Laser irradiation of 40 ns pulse duration was used. It was supposed that if pulse duration and pulse frequency are small enough, it is possible to separate in time the processes of record and erasure. After each pulse, the medium has time to pass into the state, when the opposite transition becomes impossible. It corresponds to our suppositions [17,18]. In Fig. 4 are shown the results regarding the effect on $As_{40}S_{60}$ thin films of Cu laser irradiation and the results obtained at an exposure by continuous Argon ion laser irradiation. The sensitivity and the level of saturation dependence on character of exposure (continuous or pulse) and intensity exposure is studied.

The competition of record and erasure processes is revealed in the effect known under the name "stopping - effect" [15,16].

Intensity of the mode (I) distributing in the ChVS thin film waveguide, in this case $As_{20}S_{80}$ decreases, when the part of a waveguide track is exposed to actinic irradiation (Fig. 5, curve 1) After external exposure stops the intensity of a waveguide mode is restored. The curves 2 - 6 in Fig. 5 correspond to different moments of such exposure ceasing. The greatest mode intensity damping was reached, when the external exposure preceded to the excitation of a waveguide mode. Mode intensity was restored completely, if under mode influence the external exposure ceased (Fig. 5, curve 8), or was established on a level corresponding to simultaneous effect of the both factors (Fig. 5, curve 7).

It is enough to compare saturation state on curves 1 and 8 in Fig. 5. This is equivalent to separation of processes of a record and erasure on two wavelengths. If pulse exposure and the subsequent chemical treatment is applied, the energetic gain will be considerable. In the work the exposure was done by a single-pulses with duration 40 ns on a wavelength of Phosphate neodymium glass laser (0.53 μm). The holographic diffraction gratings formed in the range of spatial frequencies 100 - 2400 mm^{-1}. Diffraction efficiency of the got elements was 45 % in the first diffraction order after metallization a grating surface .The exposure was 3×10^{-3} J/cm^2.

With the purpose to define the extreme parameters of investigated photoresists the range of the wavelength 0.45 - 0.60 μm of a recording radiation was studied. The exposure was done by single-pulses with duration 10 ns by the Dye laser. It is found out, that the latent image can be developed already at 2×10^{-4} J/cm^2. Exposure and the level of chemical strengthening were determined as a function of a holographic optical element. Thus, they can be varied in a wide range.

Apart from periodic structures such as reflective diffraction gratings in the work other types of the relief - phase holograms were obtained for usage as master matrixes in processes of mass replication of the holograms on the plastic films.

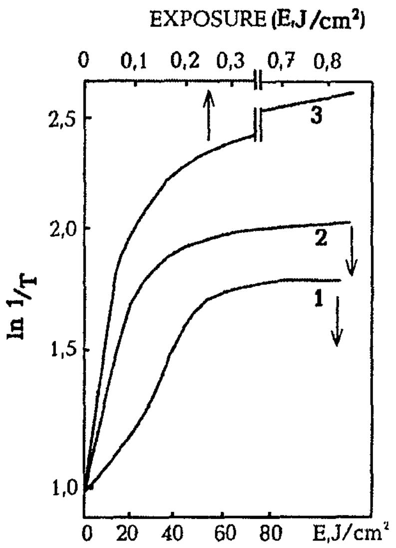

Fig. 4. Characteristic curves of the sample $As_{40}S_{60}$ thin film under band-gap irradiation 1, 2 – Argon ion laser irradiation 0.2 W/cm^2 and 1.0 W/cm^2, respectively.: 3 – Cu laser irradiation, 4x10^3 W/cm^2.

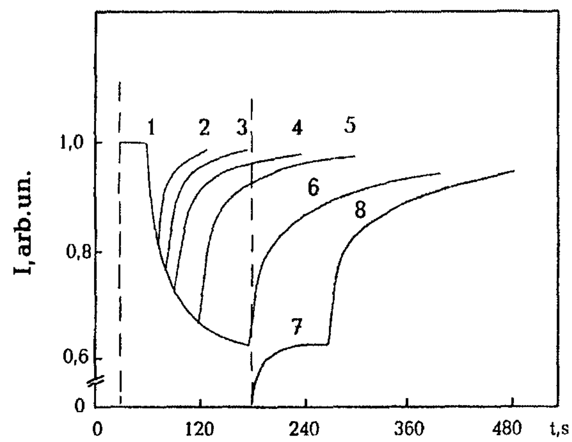

Fig. 5. Light-operated waveguide in $As_{20}S_{80}$ thin films: dynamics of switch and recovery.

4. Conclusions

In this work the prospects of usage $As_{50}Se_{50}$ thin films is shown. Such photoresist films is characterized by low exposure both in continuous, and in a pulse regime of a record and, simultaneously, high operational parameters.

On $As_{50}Se_{50}$ thin films the different kinds of holographic optical elements and holograms are realised with high diffraction efficiency.

The experimental data confirm the supposition about a competition of processes of a record and erasure during exposure of the thin ChVS films, that allows to vary the sensitivity of such materials.

The controlled vacuum deposition, repeatability and uniformity of parameters on the film surface, and the absence of deformation are characteristic to organic photoresists during the processing, and are the padding factors, which are important for future applications of the chalcogenide photoresists.

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